Chem. Eng. Technol. *14* (1991) 295 – 300

Simulation of a Distillation Column on an IBM PC, Accounting for Real Behaviour of Electrolyte Solutions*

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This contribution demonstrates the possibility of using a thermodynamic description of electrolyte solutions directly for computer simulation of distillation columns. Coefficients are determined for a combination of a solvation model with a local composition equation for the activity coefficient. The use of one set of coefficients yields good results of calculation of vapour pressure, vapour phase composition and caloric data of hydrochloric acid. Solution of material and heat balance equations of distillation columns is achieved on an IBM PC with the above description. Two illustrative examples of an absorption and a rectification calculation are presented

1 Introduction

Process design of chemical plants by computer simulation requires the knowledge of physical properties of fluids for the design of industrial equipment. Distillation columns are very important in many chemical plants. The present contribution deals with complex columns for multicomponent distillation. The simulation of distillation columns is not a new topic but, nevertheless, it leads to severe problems if electrolyte solutions are present. The description of phase equilibria of electrolyte solutions, such as hydrochloric or sulphuric acid, is difficult because of strong non-ideality of these azeotropic systems.

A program based on a thermodynamic description [2] performed on an IBM-PC for the system H_2O-HCl is used for successful simulations of distillation and absorption columns.

2 Description of Electrolyte Solutions

The thermodynamic description combines an equation for the activity coefficients (NRTL [5], Wilson [6]) with a solvation model [2], which accounts for the internal grouping within the liquid phase.

The vapour pressure of any component is calculated from[1]

$$p_i = x_i \, \gamma_i \, p_i^0 \quad , \tag{1}$$

where p_i is the partial pressure, x_i the mole fraction of the liquid phase, γ_i the activity coefficient and p_i^0 the vapour pressure of pure substance.

This includes the assumptions that the vapour behaves as an ideal gas and the liquid is incompressible. These simplifications are permissible in view of the investigated pressure range. The application of a local composition model such as the Wilson and NRTL equations for the activity coefficient gives satisfactory results only for non-electrolyte solutions.

With the introduction of a solvation model, we perform an equilibrium reaction, which alters the composition in the liquid. Both Wilson and NRTL equations use these new compositions. This model takes into account the dissociation of the electrolyte and the formation of a solvent cloud. This will be referred to as cluster C^+, C^- and is shown in Fig. 1.

Let the number of dissociation products be ν (for hydrochloric acid $\nu = 2$: H^+ and Cl^-). The total number of solvent molecules which are bound in ν clusters is denoted by m (in Fig. 1: $m = 3$). Owing to absence of ions in the vapour, vapour pressure of the clusters is neglected. For computer programs, this solvation model can be regarded as a UNIT. INPUT are the mole fractions when solvation is not considered while OUTPUT are those mole fractions when solvation is considered (Fig. 2); then $p_i = x_i \, \gamma_i \, p_i^0$.

The solvation reaction is described with an equilibrium constant K_a, which gives the missing equation for the cluster mole fraction. In total, we obtain a set of non-linear Eqs (2), (3) and (4).

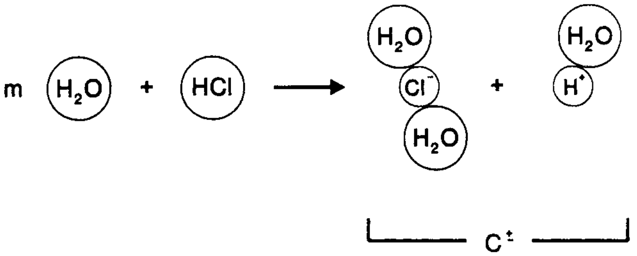

Fig. 1. Solvation model.

Fig. 2. Solvation UNIT.

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[1] List of symbols at the end of the paper.

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* Paper presented by A. Bosen at the "Jahrestreffen der Verfahrens-Ingenieure", Stuttgart, October 3 to 5, 1990.

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0930-7516/91/0510-0295 $03.50+.25/0

$$x_S = x_S^0 + x_C\left[x_S^0(m+1-\nu) - m\right] \quad , \qquad (2)$$

$$x_E = x_E^0 + x_C\left[x_E^0(m+1-\nu) - 1\right] \quad , \qquad (3)$$

$$K_a = \frac{x_C^\nu}{x_S^m x_E} \; \frac{\gamma_C^\nu}{\gamma_S^m \gamma_E} \quad . \qquad (4)$$

(Note: $1 = x_S + x_E + \nu x_C$)

2.1 Enthalpy of Solution

In order to formulate an energy balance, one needs the caloric data. Molar enthalpy of the solution must be calculated with the following equation:

$$h = \frac{1}{1 + x_C(m+1-\nu)}\left(h^E + x_C R T^2 \frac{\partial \ln K_a}{\partial T}\right) + x_S^0 h_S^0 + x_E^0 h_E^0 \quad . \qquad (5)$$

2.2 Approximation

To use the above equations, the values of γ_i, K_a and m must be known. They result from an approximation to experimental data, where coefficients (the relationship will be stated later) are adapted.

Experimental data on total pressure, vapour phase composition and caloric values were obtained to determine the coefficients by the following method.

$$\sum_i^I \left(\frac{y_i^{EXP} - y_i^{CAL}}{y_i^{EXP}}\right)^2 \overset{!}{=} \text{minimum} \quad .$$

EXP: experimental data point,
CAL: calculated value,
I: number of data points.

One set of coefficients is obtained which yields satisfactory results for all the experimental data. Several systems are described, using the solvation model e.g. [1, 3].

The quality of this description will be illustrated by a comparison of calculated and experimental data for hydrochloric acid (Fig. 3 and Table 1). The diagrams are based on the Wilson equation.

2.3 Equations and Coefficients

2.3.1 Wilson Equation [6]

Activity coefficient:

$$\ln \gamma_i = 1 - \ln\left(\sum_j^N x_j \Lambda_{ij}\right) - \sum_k^N \frac{x_k \Lambda_{ki}}{\sum_j^N x_j \Lambda_{kj}} \quad . \qquad (6)$$

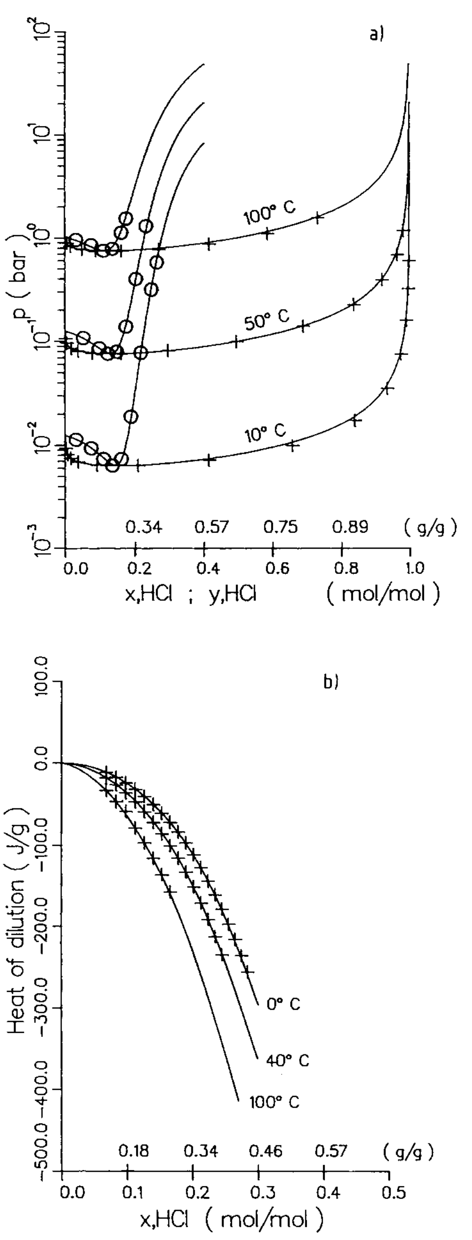

Fig. 3. Comparison of calculated (–) and experimental (+, o) values. System: H_2O-HCl.

Table 1. Experimental data of the system hydrochloric acid.
Final errors: Wilson coefficients: taken from [3], NRTL coefficients: this work.

	Number of data points	Relative deviation [%]			
		Wilson		NRTL	
		mean	max.	mean	max.
All values	534	2.3	13.0	2.6	16.8
Total pressure	275	2.2	13.0	2.6	13.6
Vapour phase composition	119	2.2	13.0	4.2	16.8
Heat of dilution	140	2.5	11.4	1.1	4.5

Molar excess enthalpy:

$$h^{\mathrm{E}} = RT^2 \sum_{i}^{N} x_i \frac{\sum\limits_{j}^{N} \frac{\partial \Lambda_{ij}}{\partial T}}{\sum\limits_{j}^{N} x_j \Lambda_{ij}} \quad , \tag{7}$$

$$\Lambda_{ij} = \exp(a_{ij} + b_{ij} T) \quad , \tag{8}$$

$$\frac{\partial \Lambda_{ij}}{\partial T} = \Lambda_{ij}\, b_{ij} \quad ,$$

$$\Lambda_{ii} = \Lambda_{jj} = 1 \quad .$$

System: Hydrochloric acid, $K_a = \exp(-7.1 + 4474/T)$.

$$\frac{\partial \ln K_a}{\partial T} = -\frac{4474}{T^2} \quad , \tag{9}$$

$\nu = 2;\ m = 4;\ N = 4$ (considering solvation).

The results are shown in Table 2.

2.3.2 NRTL Equation [5]

Activity coefficient:

$$\ln \gamma_i = \frac{\sum\limits_{j}^{N} \tau_{ji} G_{ji} x_j}{\sum\limits_{j}^{N} G_{ji} x_j} + \sum_{k}^{N} \frac{x_k G_{ik}}{\sum\limits_{j}^{N} G_{jk} x_j} \left[\tau_{ik} - \frac{\sum\limits_{n}^{N} \tau_{nk} G_{nk} x_n}{\sum\limits_{j}^{N} G_{jk} x_j} \right] \quad , \tag{10}$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad .$$

Molar excess enthalpy:

$$h^{\mathrm{E}} = -RT^2 \sum_{i}^{N} x_i \frac{u' v - v' u}{v^2} \quad , \tag{11}$$

$$u = \sum_{j}^{N} \tau_{ji} G_{ji} x_j \quad u' = \sum_{j}^{N} \left(x_j \frac{\partial \tau_{ji}}{\partial T} G_{ji} + \tau_{ji} \frac{\partial G_{ji}}{\partial T} \right) \quad ,$$

$$v = \sum_{k}^{N} G_{ki} x_k \quad v' = \sum_{k}^{N} x_k \frac{\partial G_{ki}}{\partial T} \quad ,$$

$$\tau_{ij} = a_{ij} + b_{ij}/T \quad , \tag{12}$$

Table 2. Wilson equation: Coefficients of the system H_2O (i = 1)-HCl (i = 2)–cluster (i = 3,4) [3].

i	j	a_{ij}	b_{ij}
1	2	5.351	− 0.0091
1	3,4	0.371	− 0.0014
2	1	− 1.342	0.0048
2	3,4	8.505	− 0.0289
3,4	1	5.260	− 0.0161
3,4	2	7.790	− 0.0160

$$\frac{\partial \tau_{ij}}{\partial T} = -\frac{b_{ij}}{T^2}; \quad \frac{\partial G_{ij}}{\partial T} = G_{ij} \alpha_{ij} \frac{b_{ij}}{T^2} \quad ,$$

$$\tau_{ii} = \tau_{jj} = 0; \quad \alpha_{ij} = \alpha_{ji} \quad .$$

System: Hydrochloric acid, $K_a = \exp(-8.897 + 4562/T)$.

$$\frac{\partial \ln K_a}{\partial T} = -\frac{4562}{T^2} \quad , \tag{13}$$

$\nu = 2;\ m = 2.37;\ N = 4$ (considering solvation).

Table 3 gives the results of the calculations.

3 Simulation of a Distillation Column

For the simulation, a hypothetical system is considered, represented by the model column in Fig. 4. The first stage corresponds to a condenser (partial, total or compound), the last stage to a reboiler. Each stage is assumed to be an equilibrium stage (Fig. 5).

Table 3. NRTL equation: Coefficients of the system H_2O (i = 1)-HCl (i = 2)-cluster (i = 3,4).

i	j	a_{ij}	b_{ij}	α_{ij}
1	2	− 3.164	1710.0	− 0.257
1	3,4	− 1.802	− 221.1	− 0.149
2	1	− 0.527	− 998.1	− 0.257
2	3,4	2.455	−329.4	− 0.336
3,4	1	3.722	− 1128.0	− 0.149
3,4	2	− 0.110	− 862.1	− 0.336

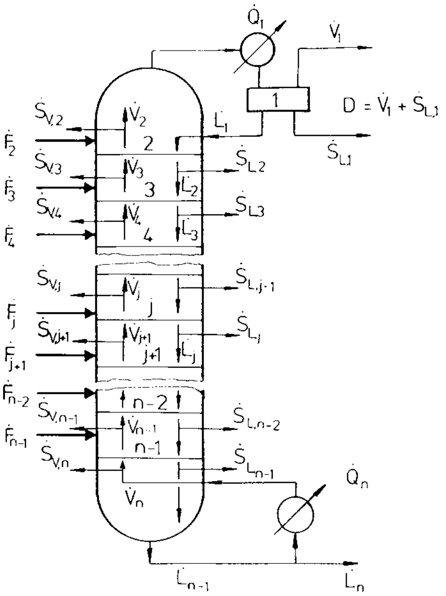

Fig. 4. Distillation column.

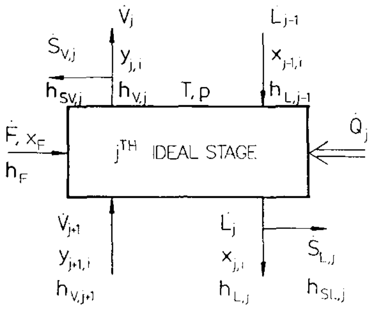

Fig. 5. Ideal equilibrium stage.

The set of equations, which must be solved for a component i, is formulated as follows:

Material balance equation around stage j

$$0 = L_{j-1}x_{i,j-1} - (V_j + S_{V,j})y_{ij} - (L_j + S_{L,j})x_{ij} + F_j x_{F,ij} \quad . \qquad (14)$$

Heat balance equation around stage j

$$\begin{aligned} 0 &= L_{j-1}h_{L,j-1} + V_{j+1}h_{V,j+1} - (V_j + S_{V,j})h_{V,j} - \\ &\quad (L_j + S_{L,j})h_{L,j} + F_j h_{F,j} + Q_j \quad . \end{aligned} \qquad (15)$$

The liquid flow rates are expressed as functions of V's by an overall material balance of all stages from condenser (stage 2) through j^{th} stage

$$L_j = V_{j+1} + \sum_{k=2}^{j} (F_k - S_{V,k} - S_{L,k}) - D \quad . \qquad (16)$$

In this paper, we assume the knowledge of feed (F, x_F), the product purities (y_1, x_n) at the condenser and the reboiler (product streams V_1, L_n from total material balance) and the reflux RF

$$\mathrm{RF} = \frac{D}{L_1} \quad . \qquad (17)$$

One may obtain a constant pressure or a pressure drop across the stage. Independent variables are the mole fractions of liquid x_{ij} ($1 \le i \le N-1$, $1 \le j \le n$) and the vapour rate profile V_3 to V_n; therefore one obtains the heats of reboiler and condenser Q_n and Q_1. For a conventional column, all other quantities of the external streams are zero.

The mole fractions of vapour phase y_{ij}, temperature T_j and enthalpy h_j are obtained from the thermodynamic description:

$$\begin{aligned} T &= f(x, p), \\ y &= f(x, T, p), \\ h &= f(x, y, T) \quad . \end{aligned}$$

Eqs (14) and (15) are solved sequentially.
The first step is to formulate an initial set of x_{ij} and V_j. Then, the non-linear equations of the material balance (14) are solved by a program from the IMSL library [4]. Values of x_{ij} are determined and used in Eq. (15); this yields new values of V_j. If the new set of values deviates (tolerance ε) from the initial set, Eq. (14) must be solved again.
After the last iteration step, the heats of condenser and reboiler are determined. The computational procedure is shown in a block diagram, Fig. 6.

3.1 *Initial Set of Values*

For the initial step, we assumed that the molar heats of vaporization of the components are equal and, for this reason, L_j and V_j are constant throughout the column; the material balance can be solved directly, the result being the initial mole fractions of liquid and the number of stages at a given reflux and the required purity of product streams.

The vapour rate profile V_j is then assumed to be linear from reboiler to condenser. The initial values are accurate enough, so that the PC program will converge.

3.2 *Illustrative Examples*

Two numerical examples for hydrochloric acid are as follows. For practical reasons, results are converted into mass related values. In the first example, a product of 99 wt-% HCl is obtained from a 28 wt-% feed.

In the second example, a stream of 17 wt-% HCl is concentrated to 31% with gaseous HCl.

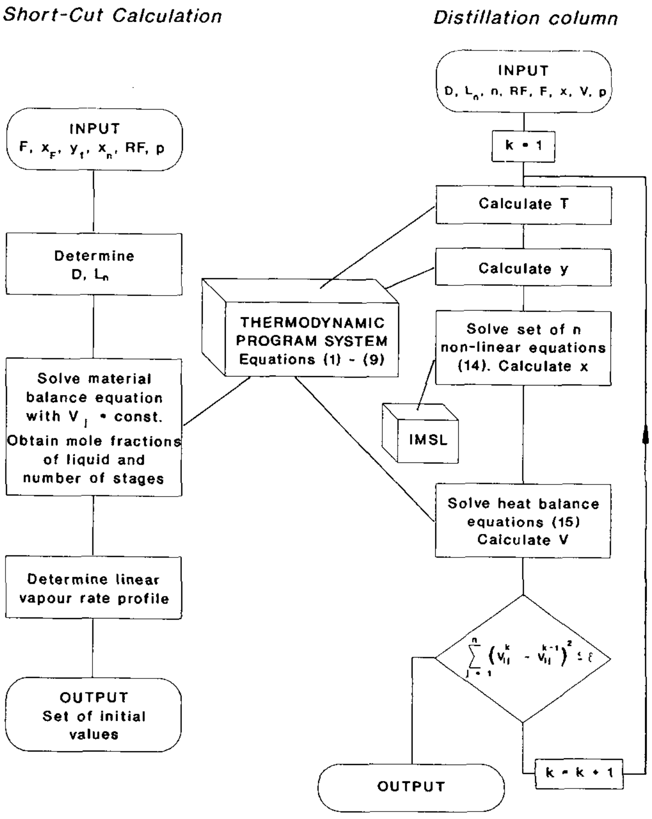

Fig. 6. Block diagram.

3.2.1 Example 1 (Figs 7 – 9)

Stage number $n = 13$; Feed stage $j = 5$; Reflux RF = 1.5.

FEED: $F = 100.0$ kg/h, $t = 96.4$ °C, $x_F = 28.3$ wt-% HCl.

PRODUCT:
Reboiler: $L_n = 90.7$ kg/h, $t = 107.7$ °C, $x_n = 21.1$ wt-%,
$Q = 29.4$ MJ/h,
Condenser: $D = 9.3$ kg/h, $t = 47.6$ °C, $y_1 = 99$ wt-%.,
$Q = 17.7$ MJ/h.

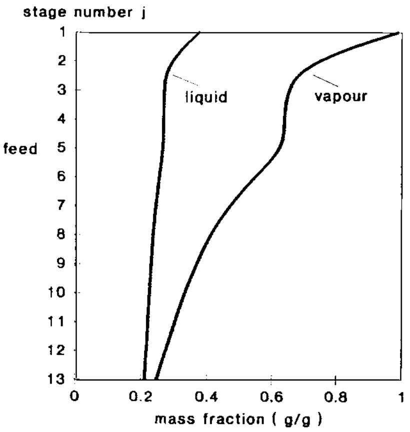

Fig. 7. Composition profiles.

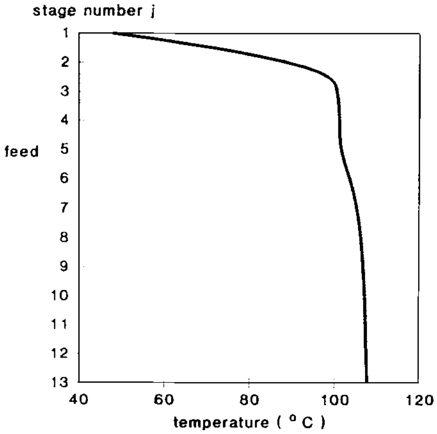

Fig. 8. Temperature profile.

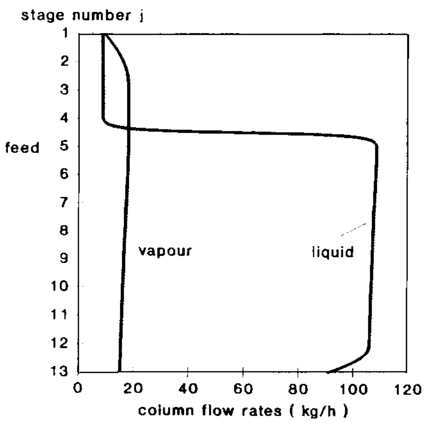

Fig. 9. Liquid and vapour mass flow rate profiles.

3.2.2. Example 2 (Figs 10 – 12)

Stage number $n = 9$, Feed 1 stage $j = 3$, Feed 2 stage $j = 9$
Reflux RF = 0.5.

FEED: $F_1 = 100.0$ kg/h, $t = 70.0$ °C, $x_F = 16.7$ wt-% HCl.
$F_2 = 19.5$ kg/h, (gaseous HCl)

PRODUCT:
Bottom: $L_n = 117.4$ kg/h, $t = 86.6$ °C, $x_n = 30.8$ wt-%,
Condenser: $D = 2.1$ kg/h, $t = 104.4$ °C, $y_1 = 1.7$ wt-%.
$Q = 2.3$ MJ/h.

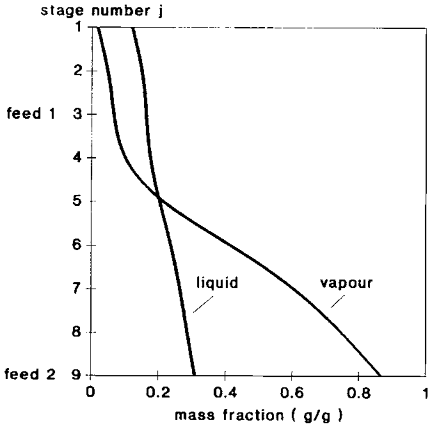

Fig. 10. Composition profiles.

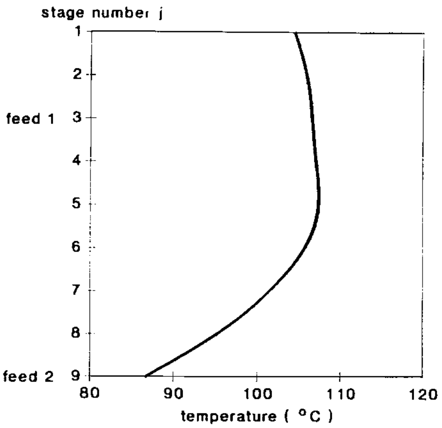

Fig. 11. Temperature profile.

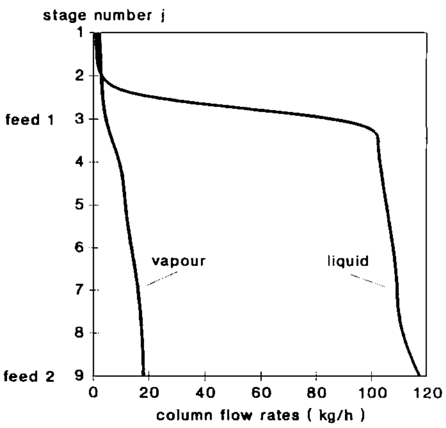

Fig. 12. Liquid and vapour mass flow rate profiles.

Received: January 2, 1991 [CET 360]

Symbols used

a_{ij}, b_{ij}	parameters in determination of activity coefficients
D	distillation rate
F	feed
G_{ij}	NRTL parameter
h	molar enthalpy
h^E	molar excess enthalpy
h_i^0	molar enthalpy of pure substance i
K_a	equilibrium constant
L_j	liquid flow rate, stage j
m	solvation number
N	number of components
n	number of stages
p_i	partial pressure
p_i^0	vapour pressure of pure component i
Q	heat duty
R	gas constant
RF	reflux
S	side stream
T	absolute temperature
t	temperature (°C)
V_j	vapour flow rate, stage j
x_i	mole fraction when solvation is considered
x_i^0	mole fraction when solvation is neglected
y_i	mole fraction of vapour phase
Y^{EXP}	experimental data (pressure, vapour composition, enthalpy)
Y^{CAL}	calculated value

Greek symbols

α_{ij}	NRTL parameter
γ_i	activity coefficient
Λ_{ij}	Wilson parameter
ν	number of dissociation products
τ_{ij}	NRTL parameter

Indices

S	solvent
E	electrolyte
C	cluster

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